Palladium Catalyzed Reaction of Trimethylsilyltributyltin with α-Halo Ketones. Preparation of Enol Silyl Ethers

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Synopsis. The reaction of trimethylsilyltributyltin with α-halo ketone in the presence of a catalytic amount of palladium chloride plus twice molar amounts of trimethyl phosphite gave enol silyl ethers in good yields.

The most important method to form Si–C bonds involves the reaction between organosilicon halides and Grignard or organolithium reagents. An alternative method available is the reaction between disilane and organic halides in the presence of appropriate transition metal complexes.[1] Application of this reaction

$$RX + Me_3SiSiMe_3 \xrightarrow{[M]} RSiMe_3 + Me_3SiX$$

to α-halo ketone was recently reported by Moro-oka *et al.* to give the reductive dehalogenated product, ketone as a major product, except for the reaction with α-bromoacetophenone which gave enol silyl ether as a major product.[2]

Comparing with hexamethyldisilane, trimethylsilyltributyltin is expected to be a more reactive reagent, because Sn–Si bond is weaker than Si–Si bond. We carried out the palladium-catalyzed reaction of trimethylsilyltributyltin with α-halo ketones under various conditions, intending to increase the yield of enol silyl ether, and to reduce the yield of reductive dehalogenated product. This note which describes the results affords an example of the catalytic silylation of α-halo ketones by means of the compound related to disilane, although a number of other methods for the preparation of enol silyl ether are so far known.[3]

$$-\overset{\overset{O}{\|}}{\underset{|}{C}}-\underset{|}{C}-X + Bu_3SnSiMe_3 \xrightarrow{[Pd]} -C=\overset{OSiMe_3}{C} + Bu_3SnX$$

The reaction of trimethylsilyltributyltin with α-bromoacetophenone in the presence of tetrakis(triphenylphosphine)palladium was carried out at various reaction temperature. As Table 1 shows, lower the temperature, the yield of α-trimethylsiloxystyrene increased comparing with that of acetophenone, the reductive dehalogenated product. The optimum temperature was about 80 °C.

The distribution of the products depended also on the nature of the catalysts and the ligands used. As shown in Table 2, the best catalyst was π-allylpalladium or palladium chloride plus twice molar amounts of trimethyl phosphite. From the view point of availability and stability of the catalysts, palladium chloride plus trimethyl phosphite may be the most recommendable catalyst.

Since, under these conditions, α-trimethylsiloxystyrene was produced in good yield and the production of acetophenone was essentially suppressed, the method was applied to the reaction with various α-halo ketones, giving the results as shown in Table 3. Enol silyl ethers were produced in good yields together with a quite small amount of the reductive dehalogenated products. The yield descended as the halo ketone varied from primary to secondary, and then to tertiary. At lower reaction temperature, the yields of the product from secondary or tertiary bromide seemed to be improved.

The mechanism for this reaction may be analogous to that proposed by Moro-oka *et al.*[2]

Table 1. Temperature dependence of products distribution

$$Bu_3SnSiMe_3 + BrCH_2COPh \xrightarrow[0.01\ mmol]{Pd(PPh_3)_4} PhC(OSiMe_3)=CH_2 + PhCOMe$$

1.2 mmol 1.0 mmol I II

Temp/°C	Yield of products/%[a] I	II
120	35	37
100	52	31
80	61	27
60	56	23

a) GLC yield based on halide. b) Solvent: PhH, 0.5 ml, reaction time: 5 h.

Table 2. Effect of the catalyst on the yield and distribution of the products

$$Bu_3SnSiMe_3 + BrCH_2COPh \xrightarrow[0.01\ mmol]{[M]} PhC(OSiMe_3)=CH_2 + PhCOMe$$

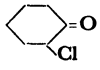
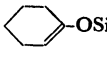
1.2 mmol 1.0 mmol I II

Catalyst	Yield of products/%[a] I	II
None	0	8
$Pd(PPh_3)_4$	61	27
$PdCl_2(PPh_3)_2$	29	19
$PdCl_2[P(o\text{-tolyl})_3]_2$	4	27
$PdCl_2[P(p\text{-tolyl})_3]_2$	51	18
$PdCl_2(PhCN)_2$	Trace	7
$RhCl(PPh_3)_3$	Trace	30
$NiCl_2(PPh_3)_2$	0	9
$[PdCl(C_3H_5)]_2$[b]	13	24
$+2P(OEt)_3$	80	13
$+2P(OPh)_3$	53	35
$+2P(OMe)_3$	76	5
$PdCl_2$[b]	Trace	3
$+2P(OEt)_3$	78	10
$+2P(OPh)_3$	15	26
$+2P(OMe)_3$	81	8
$Pd(OAc)_2$[b] $+2P(OEt)_3$	48	18

a) GLC yield based on halide. b) Used 0.05 mmol. c) Solvent: PhH, 0.5 ml, reaction time: 5 h.

Table 3. Pd-catalyzed reaction of trimethyltributyltin with various α-halo ketones

$Bu_3SnSiMe_3$ + α-Halo ketone $\xrightarrow{[M]^{a)}}$ Enol silyl ether + Bu_3SnX
36 mmol 30 mmol

α-Halo ketone	Yield of product/%[b]		Bp θ_b/°C (mmHg)
$BrCH_2COMe$	$CH_2=C(OSiMe_3)Me$	80(67)[d]	94
$BrCH_2COEt$	$CH_2=C(OSiMe_3)Et$	89(72)[d]	114
$BrCH_2CO^iPr$	$CH_2=C(OSiMe_3)^iPr$	93	
$BrCH_2CO^tBu$	$CH_2=C(OSiMe_3)^tBu$	95(75)	70(70)
$BrCH_2COPh$	$CH_2=C(OSiMe_3)Ph$	76(69)	102(20)
		52	
MeCOCHBrMe	$Me(Me_3SiO)C=CHMe$	50(73)[c,d]	124
$MeCOCHBrMe_2$	$Me(Me_3SiO)C=CMe_2$	30(40)[c,d]	60(70)

a) $PdCl_2$ (0.3 mmol) + $2P(OMe)_3$ in PhH (10 ml) at 80 °C for 5 h. b) GLC yield based on halide, isolated yield in parentheses. c) At 60 °C for 24 h. d) Solvent: tetralin, 10 ml.

Experimental

Boiling points are uncorrected. IR spectra were recorded on a Hitachi EPI-3G spectrophotometer. NMR spectra were recorded on a Varian EM-360 instrument. GLC analyses were carried out with an Ohkura 802 instrument, using columns (1.5 m) packed with 10% Silicone SF-96, 10% SE-30, 10% Apiezon Grease L, or 10% Carbowax-20M on Celite 545 (AW DMCS).

Materials. Trimethylsilyltributyltin,[4] bromoacetone,[5] 1-bromo-2-butanone and 3-bromo-2-butanone,[6] 1-bromo-3-methyl-2-butanone and 3-bromo-3-methyl-2-butanone,[6] 1-bromo-3,3-dimethyl-2-butanone,[7] α-bromoacetophenone,[8] 2-chlorocyclohexanone,[9] $Pd(PPh_3)_4$,[10] $PdCl_2(PPh_3)_2$,[11] $PdCl_2[P(o\text{-}tolyl)_3]_2$,[11] $PdCl_2[P(p\text{-}tolyl)_3]_2$,[11] $PdCl_2(PhCN)_2$,[12] $RhCl(PPh_3)_3$,[13] $NiCl_2(PPh_3)_2$,[14] and $[PdCl(C_3H_5)]_2$[15] were prepared by the methods described in literatures.

Reaction Procedures. Solutions of trimethylsilyltributyltin (1.2 mmol), α-halo ketone (1.0 mmol), and the catalyst (0.01 mmol) in benzene (0.5 ml) were degassed and sealed *in vacuo*. After heating for 5 h, the reaction mixtures were subjected in GLC. For the experiment in preparative scale, solutions of 30 times amounts of reactants and catalyst were prepared and heated under argon at 80 °C for 5 h. The products were isolated by distillation under reduced pressure.

Products. All the products are known compounds,[16,17] identification of which was based on their spectroscopic data recorded here.

2-Trimethylsiloxy-1-propene: IR (neat) 1640 and 900 (C=C), and 1030 cm^{-1} (Si–O–C). ^1H NMR (CCl_4) δ=0.18 (s, 9H), 1.72 (s, 3H), and 3.95 (s, 2H).

2-Trimethylsiloxy-1-butene: IR (neat) 1620 and 880 (C=C), and 1030 cm^{-1} (Si–O–C). ^1H NMR (CCl_4) δ=0.13 (s, 9H), 0.92 (t, J=7.6 Hz, 3H), 1.93 (q, J=7.6 Hz, 2H), and 3.89 (s, 2H).

2-Trimethylsiloxy-3-methyl-1-butene: IR (neat) 1630 and 860 (C=C), and 1010 cm^{-1} (Si–O–C). ^1H NMR (CCl_4) δ=0.20 (s, 9H), 0.96 (d, J=6 Hz, 6H), 2.10 (h, J=6 Hz, 1H), 3.84 (s, 1H), and 3.95 (s, 1H).

2-Trimethylsiloxy-3,3-dimethyl-1-butene: IR (neat) 1620 and 880 (C=C), and 1030 cm^{-1} (Si–O–C). ^1H NMR (CCl_4) δ= 0.18 (s, 9H), 1.05 (s, 9H), 3.85 (d, J=1 Hz, 1H), and 4.01 (d, J=1 Hz, 1H).

α-Trimethylsiloxystyrene. IR (neat) 1620 (C=C) and 1010 cm^{-1} (Si–O–C). ^1H NMR (CCl_4) δ=0.26 (s, 9H), 4.27 (d, J=1.7 Hz, 1H), 4.73 (d, J=1.7 Hz, 1H), and 7.00—7.58 (m, 5H).

1-Trimethylsiloxycyclohexene: IR (neat) 1670 and 898 (C=C), and 1190 cm^{-1} (Si–O–C). ^1H NMR (CCl_4) δ=0.15 (s, 9H), 1.31—1.73 (m, 4H), 1.73—2.18 (m, 4H), and 4.73 (m, 1H).

2-Trimethylsiloxy-2-butene: IR (neat) 1680 and 900 (C=C), and 1050 cm^{-1} (Si–O–C). ^1H NMR (CCl_4) δ=0.18 (s, 9H), 1.43 (d, q, J=6.6 and 1 Hz, 3H), 1.71 (m, 3H), and 4.41 (q,q, J=6.6 and 1 Hz, 1H).

2-Trimethylsiloxy-3-methyl-2-butene: IR (neat) 1680 and 905 (C=C), and 1010 cm^{-1} (Si–O–C). ^1H NMR (CCl_4) δ=0.10 (s, 9H), 1.55 (s, 6H), and 1.70 (s, 3H).

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